

# (12) UK Patent Application (19) GB (11) 2 360 525 (13) A

(43) Date of A Publication 26.09.2001

(21) Application No 0007138.1

(22) Date of Filing 24.03.2000

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(51) INT CL<sup>7</sup>

**C09D 179/02**

(52) UK CL (Edition S )

**C3V VACM**  
**C3W W330**  
**U1S S1397 S1574 S1814**

(56) Documents Cited

**WO 98/31719 A** **WO 98/31539 A** **WO 86/07072 A**  
**US 5120363 A**

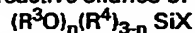
(58) Field of Search

**UK CL (Edition R ) C3V VABF VACF VACM**  
**INT CL<sup>7</sup> C08G , C09D**  
**ONLINE - WPI, EPODOC, PAJ, CAS ONLINE**

(54) Abstract Title

**Barrier coatings**

(57) The invention provides a process for treating a surface of a substrate with a composition comprising:- the reaction product of an amino-functional organic polymer, preferably a polyethylenimine and a reactive silane or a mixture of reactive silanes of the formula:



in a non-aqueous solvent, by applying the composition on to the surface to form a layer and curing the layer in the presence of moisture.

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BARRIER COATINGS

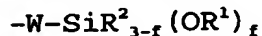
This invention relates to the preparation of barrier coatings on films and particularly coatings containing amino-  
5 functional organic polymer.

A wide variety of amino-functional organic polymer based coating compositions have been proposed as coatings for substrates, such as organic polymer films, for use in the packaging industry. These coatings may, for example improve  
10 the gas, oil, and/or flavour barrier performance of organic polymer film substrates. Furthermore, both the adhesion of coatings of this type to a film surface, and the barrier characteristics provided by the coating are known to be greatly enhanced by exposing the coated film to electron beam  
15 radiation.

WO98/31719 discloses a composition comprising an ethylenically unsaturated acid, a polyamine and additionally a crosslinking molecule, for example a multifunctional silane or organic molecule such as an acrylate for the provision of  
20 a gas, flavour and aroma barrier. WO 98/31539 discloses a method of laminating two substrates together by means of a laminating adhesive composition comprising an ethylenically unsaturated acid, a polyamine and optionally a crosslinking molecule, for example a multifunctional silane or organic  
25 molecule such as an acrylate. In both WO98/31719 and WO 98/31539 the compositions disclosed are preferably cured by free radical initiation, for example by ultraviolet, electron beam or gamma radiation or alternatively by means of chemical free radical initiators such as azo compounds or peroxides.  
30 Furthermore both WO98/31719 and WO 98/31539 teach that the presence of ethylenically unsaturated acids is absolutely essential for the success of the coatings prepared as described therein.

European patent application No 99119359.0 discloses a  
35 gas barrier composition comprising:

(A) an alkoxysilyl functional polyamine compound, or a hydrolyzate thereof, said polyamine compound having three or more amine groups, at least one nitrogen atom of said amine groups being bonded to a hydrogen atom and at least one nitrogen of said amine groups being bonded to an alkoxysilyl group expressed by the formula



wherein  $R^1$  is an alkyl group having 1 to 6 carbon atoms,  $R^2$  is a monovalent hydrocarbon group having 1 to 10 carbon atoms,  $W$  is a divalent hydrocarbon group having 2 to 10 carbon atoms, and  $f$  is an integer having a value of 1 to 3; and

(B) an organic compound which is free of acrylic groups, said organic compound having an aromatic ring or an alicyclic hydrocarbon group and having per molecule at least two functional groups that are reactive with the amine groups, the alkoxy groups, or both, of component A.

The present inventors have surprisingly discovered that one may treat a surface of a substrate to provide commercially acceptable barrier properties by use of a composition comprising an amino - functional organic polymer to which silane groups are attached but which contains no ethylenically unsaturated acid.

The present invention provides in one of its aspects a process for treating a surface of a substrate with a composition comprising:-

the reaction product of an amino-functional organic polymer comprising units of the formula  $-R^2 - N(R^1)_2$  and/or units of the formula  $R^1 - N(R^2-)_2$ , wherein each  $R^1$  is the same or different and represents a radical selected from the group consisting of hydrogen, alkyl, hydroxy alkyl, aryl substituted hydroxy alkyl, aryl, arylalkyl, and alkylaryl, and each  $R^2$  is the same or different and represents a radical selected from the group consisting of linear or branched alkylene groups having 1 to

18 carbon atoms and arylene groups having from 6 to 18 carbon atoms, and

a reactive silane or a mixture of reactive silanes of the formula:



where each  $R^3$  group is the same or different and represents a radical selected from the group consisting of an alkyl group having from 1 to 4 carbon atoms and an acyl group  $(RC(O)-)$  having from 1 to 4 carbon atoms, each  $R^4$  group is the same or

10 different and represents a hydrocarbon group with from 1 to 8 carbon atoms, X represents an organic radical having at least one functional unit selected from the group of an epoxide, an aldehyde, an episulphide, an acrylate, a methacrylate, an acrylamide, a methacrylamide, an isocyanate, an  
15 isothiocyanate, a halogen atom and an acid chloride and  $n$  is 1, 2 or 3,

in a non-aqueous solvent,

wherein said composition does not include an ethylenically unsaturated acid;

20 said process comprising applying the composition on to the surface to form a layer and curing the layer in the presence of moisture.

The concept of "comprising" where used herein is used in its widest sense to mean and to encompass the notions of  
25 "include", "comprehend" and "consist of".

In a process according to the invention the amino-functional organic polymer comprises units of the formula -  $R^2 - N(R^1)_2$ , and/or units of the formula  $R^1 - N(R^2-)_2$ , however, groups of the formula

30  $(-R^2)_3N$  may also be present in the amino-functional organic polymer wherein  $R^2$  is as defined above.

The amino-functional organic polymers suitable for use in the present invention preferably have molecular weights of from 150 to 2,000,000, with 400 to 100,000 preferred, and  
35 most preferred being from 600 to 25,000. Amino-functional organic polymers having higher degrees of polymerization tend

to provide a lower degree of tackiness in the final composition. The lower molecular weight amino-functional organic polymers can be further polymerized to form higher molecular weight amino-functional organic polymers by methods well known in the art, for example by reaction with dialkyl halides (i.e. ethylene dichloride), diisocyanates (e.g. tolyldiisocyanate, hexamethylene diisocyanate), di(meth)acrylate esters (e.g. hexene diol diacrylate, pentaerythritol diacrylate), diepoxides (ethylene glycol diglycidyl ether, vinylcyclohexene diepoxide).

Examples of amino-functional organic polymers suitable for use in the invention include polyvinyl amines, amino-functional polyacrylamides, poly(diallyldimethylammonium chlorides), polyvinyl pyrrolidone copolymers, polyalkylenimine and the reaction product of ethylene diamine and epichlorohydrin and dendrimeric amino-functional organic polymers, for example the polypropylenimines and polyamidoamines.

The most preferred amino-functional organic polymers which may be used to achieve varying degrees of tackiness are the class of amino-functional organic polymers referred to as polyalkylenimines, for example polyethylenimines, which are readily available in a wide range of molecular weights and different degrees of branching. Polyethylenimines consist of a large family of water-soluble, i.e. hydrophilic, amino-functional organic polymers of varying molecular weight and degree of chemical modification. It is generally known that the polymerization of ethylenimine does not result in a polymer composed of units having a completely linear structure, but in a polymer having a degree of branching, depending on the initiator type, concentration, temperature and pressure conditions during polymerization. The degree of branching may vary between 12 and 38 percent. The formula of polyethylenimine can be represented in the form of A, B, or C units, where:

A is an  $-R^2 - N(R^1)_2$  unit, B is an  $R^1 - N(R^2)_2$  unit, and C is an  $(-R^2)_3N$  unit,

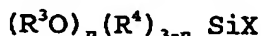
where  $R^1$  is hydrogen and  $R^2$  is an ethylene group. The ratio of A to B to C units may be from 1:0.5:0.5 to 1:2:1, but is preferably from 1:1:1 to 1:2:1.

Additional groups may be added onto polyethylenimines using methods well known in the art, to change the affinity of the coating to the substrate, or the adhesive properties.

Examples of polyethylenimine modification include reaction with ethylene oxide structures (ethylene oxide, glycidol) to introduce hydroxyl groups.

Preferred polyethylenimines have a molecular weight of from 600 to 80,000. Most preferred are polyethylenimines have a molecular weight of from 600 to 25,000.

In a process according to the invention the or each reactive silane has the formula:



Each  $R^3$  group may be an alkyl group having from 1 to 4 carbon atoms. Most preferably  $R^3$  is a methyl or ethyl group.

Each  $R^4$  group may be an alkyl group or a linear, cyclic or branched alkylaryl group. Preferably  $n$  is 2 or 3, most preferably  $n$  is 3.

Most preferred reactive silanes are where  $n$  is 3 and each  $R^3$  group is a methyl or ethyl group, in which case the reactive silane is a trialkoxysilane group which may undergo a hydrolysis and/or condensation reaction subsequent to coating the composition of the present invention by adding water in-situ. Furthermore, as the silane portion of the molecule is terminated with alkoxy groups, it can condense with the alkoxy portion of other silicone terminated molecules to form Si-O-Si groups. The resulting Si-O-Si bonds increase the crosslink density of the composition.

Specific examples of the reactive silane may be selected from gamma-acryloxypropyl trimethoxysilane, gamma-methacryloxypropyl trimethoxysilane, 3-glycidoxypropyl trimethoxysilane, chloropropyl trimethoxysilane, chloropropyl

triethoxysilane, chloropropyl methyl dimethoxy silane  
chloropropyl ethyldimethoxy silane,  
epoxycyclohexylethyltrimethoxysilane, gamma  
trimethoxysilylpropyl glycidyl ether and glycidoxypropyl  
5 methyldimethoxy silane.

The most preferred reactive silanes are chloropropyl  
trimethoxysilane and chloropropyl triethoxysilane and gamma  
trimethoxysilylpropyl glycidyl ether.

A non-aqueous solvent suitable for use in the present  
10 invention is an alcohol, for example methanol, ethanol, n-  
propanol, isopropanol, butanol, and 1-methoxy-2-propanol or  
mixtures thereof, the most preferred being ethanol and  
isopropyl alcohol. Alternative solvents which may be utilised  
include an ether, for example ethyl ether, an ester, for  
15 example ethyl acetate, a hydrocarbon, for example  
cyclohexane, and ether derivatives of mono or polyglycols,  
for example mono or polyalkylene oxides, for example ethylene  
glycol dimethyl ether.

The selected solvent must be able to wet the substrate  
20 onto which the composition is to be applied. Preferably, the  
solvent is non-toxic, and does not extend the drying time of  
the layer beyond a commercially acceptable period.

The amount of solvent may range from about 1 to about 99  
parts by weight and is preferably from about 50 to about 95  
25 parts by weight of the total composition. Water should be  
excluded from these solvents to ensure stability of the  
coating formulation.

Optionally an additional crosslinking agent may be  
utilised in the composition as described above. Cross-linking  
30 agents suitable for the present invention may be selected  
from the group of one or more multifunction silanes and/or  
one or more organic crosslinkers.

As used herein the term " additional crosslinking agent"  
is defined as an agent which can further chain extend and/or  
35 crosslink the amino-functional organic polymer/ reactive  
silane reaction product. The additional crosslinking agent

may be added with a view to improving barrier properties, adhesive properties, reducing dewetting, and/or improving appearance. It is believed that a higher crosslink density causes these improved properties.

5       The multifunctional silane may, for example be a reactive silane as defined above or a compound which imparts silane functionality and which can further cause crosslinking to form a siloxane resin network through the condensation of the silane functionality, for example tetraethyl  
10 orthosilicate, polydiethoxysiloxane (PDEOS), and disilyl compounds for example, bis(trimethoxysilylpropyl)amine.

      The organic crosslinker may be one or more compounds useful to chain extend and crosslink amino-functional organic polymer/ reactive silane reaction product and may be  
15 selected from the group of multifunctional acrylates or methacrylates, epoxides, isocyanates, thiocyanates, acid halides, acid anhydrides, esters, alkyl halides, aldehydes or combinations thereof. Specific examples include, but are not limited to hexanediol diacrylate, glycidyl methacrylate,  
20 ethyleneglycoldiglycidyl ether, and tolyl di-isocyanate.

      Particularly preferred are compounds which will undergo an acid catalyzed condensation reaction with the nitrogen atom of the amino-functional organic polymer, for example tris-methylol phenol, formaldehyde, glyoxal, p-benzoquinone,  
25 and mixtures of formaldehyde and active methylene compounds that will undergo a Mannich reaction.

      The reaction product may be prepared by mixing the amino-functional organic polymer, reactive silane and solvent in any order. However, it is preferred that the reactive  
30 silane is added to a solution of the amino-functional organic polymer in an appropriate solvent.

      The reactive silane is preferably added in an amino-functional organic polymer to reactive silane weight ratio of from 10:1 to from 1:10, with a preferred ratio being from  
35 4:1 to 1:4 and most preferred ratio being 2:1 to 1:2.



Where necessary the reaction product may be neutralised prior to use of the composition. This is particularly important in cases where the functional unit of X in the reactive silane is a halogen, for example when the reactive silane is chloropropyltrimethoxysilane. In these cases the reaction of the reactive silane with the amino-functional organic polymer, for example a polyethylenimine, results in the formation of a hydrochloride salt which is preferably neutralised to obtain the free polymer product. Any appropriate base may be used for the neutralisation step, however a methanolic solution of sodium methoxide or an ethanolic solution of sodium ethoxide is preferred as the neutralisation process results in the production of a precipitate of sodium chloride which may be easily filtered off.

The additional crosslinking agent when required may be added in an amino-functional organic polymer/organic crosslinker ratio of 100:1 to 1:1, with a preferred ratio being 10:1 to 2:1.

Preferably the additional crosslinking agent may be added to the reaction product either prior to or subsequent to coating the composition in accordance with the present invention onto a substrate.

Various optional additives may also be added to the composition to improve various properties as required. These additives may be added in any suitable amount provided they do not degrade the performance of the barrier coatings as illustrated herein. Such additives include condensation catalysts, for example tin and titanium compounds or amines, which may be utilised to assist cure speed and fillers selected from, for example silica, magnesium oxide, clay, diatomaceous earth, calcium carbonate, finely ground quartz and nanoparticles. Silicon containing nanoparticles such as silicates, for example exfoliated vermiculite, montmorillonite and apophyllite, may be added to the compound in order to reduce the thickness and/or weight of the

resultant coating. This would be particularly useful if the nanoparticles were exfoliated after having been thoroughly mixed into a compound or mixture prior to applying the layer to the substrate.

- 5        Other possible additives include antiblock and slip  
aides, for example stearamide, oleamide or polar additives,  
for example epoxides, acrylates, methacrylates, polyols,  
glycidol, glycidyl methacrylate, ethylene glycol  
diglycidylether, bisphenol A diglycidylether, or amino-  
10 functional organic polymers, for example polyethylenimine and  
other silanes. Wetting agents, for example polyethoxylated  
phenol may also be added.

15        The polar additives may be used with a view to creating  
an increase in polarity, for example by adding OH groups onto  
the reaction product by reaction of the polyethylenimine with  
epoxides.

20        In a process according to the invention the layer may be  
applied on to a wide variety of substrates, including, but  
not limited to polyolefins, including oriented polypropylene  
(OPP), cast polypropylene, polyethylene, polystyrene;  
polyolefin copolymers, including ethylene vinyl acetate,  
ethylene acrylic acid, ethylene vinyl alcohol (EVOH),  
ionomers, polyvinyl alcohol and copolymers thereof;  
polyacrylonitrile; polyvinyl chloride, polyvinyl dichloride,  
25 polyvinylidene chloride and polyacrylates.

      Further alternative substrates include polyesters, for  
example polyethylene terephthalate (PET) or polyethylene  
naphthalate (PEN); polyamides, for example nylon and MXD6  
and polyimides.

30        Even further possible substrates include  
polysaccharides, for example regenerated cellulose, glassine  
or clay coated paper, paperboard or Kraft paper or  
metallised polymer films and vapour deposited metal oxide  
coated polymer films, for example  $AlO_x$ ,  $SiO_x$ , or  $TiO_x$ .

In a process in accordance with the invention the layer applied according to the invention may be applied to the aforesaid substrates when they are in the form of a film or sheet or moulding, though this is not obligatory. The  
5 substrate may be selected from a copolymer, a laminate, a blend, a coating or co-extruded or a combination of any of the substrates listed above according to the compatibility of the materials concerned with each other. In addition, the  
10 substrate may be in the form of a rigid container made from materials, for example polyethylene, polypropylene, polystyrene, polyamide, PET, polymers of EVOH, or laminates containing such materials.

In a process according to the invention the layer may be applied onto a substrate in any desired amount, however, it  
15 is preferred that the layer be applied in an amount suitable to form a coating weight on the substrate of from about 0.05 to about 20 g/m<sup>2</sup>. Preferably the coating weight is from about 0.5 to about 10 g/m<sup>2</sup>, and most preferably is from 0.5 to 5g/m<sup>2</sup>. Coating weights may be determined by gravimetric  
20 comparison. The layer may be applied to the substrate by any conventional process, for example spray coating, roll coating, slot coating, meniscus coating, immersion coating, and direct, offset, and reverse gravure coating.

The layer of the composition may be cured via a  
25 condensation reaction, which requires the presence of moisture. The moisture may be added through steam or in a high humidity oven (preferred relative humidity (RH) level: 40 to 100% most preferred: 60 to 80%). It is, however to be noted that wherever possible water should be excluded from  
30 the composition prior to commencement of the cure process to avoid premature curing (gelling).

The curing reaction may be accelerated by the application of heat, for example by heating in an oven at temperatures up to a maximum of about 140°C. The curing  
35 process is preferably undertaken at temperatures of from 50°C to 120°C, temperatures from 60°C to 100°C being most

preferred. Heating time is temperature and air-velocity dependent and the coating will reach tack free time in one second to 10 minutes depending on drying conditions. The heating step serves to evaporate the solvent, and accelerate  
5 the condensation reaction between silanol groups.

Whilst in a process according to the present invention the composition is applied on to a substrate to form a layer prior to curing when it is exposed to moisture, the composition may alternatively be used as a laminate adhesive,  
10 i.e. the composition may be applied to form a layer on a first substrate it may be used and optionally laminated to another substrate before complete drying. The invention can be applied as a coating or as an adhesive to a variety of substrates used in various applications, including laminated  
15 films for the packaging of food and non-food products.

If desired, substrates used in a process according to the invention may be pretreated prior to application of the layer, for example by corona treatment, plasma treatment, acid treatments and/or flame treatments, all of which are  
20 known in the art. Furthermore, any of the foregoing substrates may have a primer or primers applied thereon prior to application of the layer. The primers may be applied to the substrates by any appropriate process known in the art, for example spray coating, roll coating, slot coating,  
25 meniscus coating, immersion coating, and indirect, offset, and reverse gravure coating and extrusion coating. Suitable primers may include, but are not limited to carbodiimide, polyethylenimine, and silanes, for example N-(2-aminoethyl)-3-aminopropyltrimethoxy silane and  
30 aminopropyltriethoxysilane.

Substrates treated by a process according to the invention may be subsequently used without further treatment. However, it is possible to bring a second substrate as described above, into contact with a first substrate under  
35 adhesive bond forming conditions, in which case the compound alone or in combination with other additives serve as a

primer or adhesive. When two substrates are present, the application of the compound and the first and second substrates may be in a continuous process where the application of the compound onto the first substrate and the second substrate onto the compound occurs substantially simultaneously. Alternatively a stepwise process may be utilised wherein the layer is initially applied onto the first substrate and subsequently the second substrate is applied onto the layer.

In addition, the process of the present invention can be used to provide barrier layers on a wide variety of packaging containers, for example pouches, tubes, bottles, vials, bag-in-boxes, stand-up pouches, gable top cartons, thermo-formed trays, brick-packs, boxes, cigarette packs and the like.

Of course, the present invention is not limited to just packaging applications, and may be used in any application wherein gas, or aroma barrier properties are desired, for example tires, buoyancy aides, inflatable devices generally, etc.

A coating resulting from the process according to the invention may be employed to improve resistance of the material to permeation of gases and aromas, for example a 30 micron corona treated low density polyethylene film is generally found to have a permeability to ethyl acetate of 700 g/m<sup>2</sup>.day as measured with permeability cups (modification of ASTM standard E96) measured at 40-60% relative humidity. With the present coatings, the ethyl acetate transmission rate of the same film can be reduced to less than 50 cc/m<sup>2</sup>.day as measured at 40-60% relative humidity.

One major advantage of the present invention over recent prior art is that no ionising radiation, for example electron beam or ultra violet radiation is required to cure the layer.

In a preferred embodiment of the invention, a quantity of the reaction product is prepared by adding 1 part of glycidoxypropyltrimethoxysilane to 1 part of Lupasol FG (a

polyethylenimine polymer from BASF) in 2 parts of isopropyl alcohol (50% solution). The solution is then coated onto a corona treated low density polyethylene and dried in a moisturised oven at 60°C before applying a second layer of low density polyethylene on the coated one with a roller. The resulting laminate is then allowed to dry fully to complete cure. Solutions are coated on the prime film to give coat weight of 3-5 g/m<sup>2</sup>.

In order that the invention may become more clear there now follows a detailed description of several coatings prepared in accordance with the present invention.

Example 1.

In this example and all subsequent Examples the results were obtained through utilisation of the following test method for analysis of ethyl acetate:-

The data was generated using a modification of ASTM standard E 96 recommended for the measure of water vapor transmission of materials. Test dishes having a mouth diameter of 35.68 mm (area 10 cm<sup>2</sup>) were used, and a minimum of 2 film samples were tested at the same time to determine reproducibility. Each dish was filled with 1 (+/-) 0.3 g of ethyl acetate, covered with the coated film, or laminate sample, sealed with Dow Corning High Vacuum silicone grease and lids were screwed tightly in order to prevent the escape of ethyl acetate other than through the coated film or laminate. The Weight of each sealed test dish containing ethyl acetate is recorded at the start of the test and thereafter is recorded every 24 hours until a constant weight loss is obtained.

The aroma barrier values for each film are given in units of grams of ethyl acetate lost per square meter of film within a 24 hours period (g/m<sup>2</sup>.d). The Ethyl Acetate transmission rate was measured in each example at between 35 and 55% Relative Humidity.

Table 1 shows the results of the above test on a variety of uncoated substrates for comparative purposes with subsequent examples. All subsequent tests were carried out on a low density polyethylene (LDPE) substrate and details of the type of coating tested are indicated in the comments column of the relevant Tables.

Table 1. Uncoated substrates

Substrate	Thickness ( $\mu\text{m}$ )	Ethyl Acetate Transmission Rate (EATR) ( $\text{g}/\text{m}^2$ per day (d))
Low density polyethylene (LDPE)	30	700
High density polyethylene (HDPE)	60	67
Oriented polypropylene (OPP)	30	70
(Aluminium vacuum coated) metallised polypropylene (Met OPP)	20	50
Polyethylene terephthalate (PET)	12	3
Aluminium Foil	15	<2

10 Example 2

This example is a further comparative example which shows the level of ethyl acetate lost from an LDPE laminate with a commonly used two part polyurethane adhesive. It is to be understood that whilst the EATR is significantly reduced compared to an uncoated sample of LDPE, the EATR is still significant. The adhesion tests to which the following table refers were carried out by merely pulling the coating and substrate apart.

The laminate was prepared as follows:-

20 A solution of 60g. of Adcote 301A and 40g. of Adcote 350A (both obtained from Morton), was prepared in 86g. of

HPLC grade ethyl acetate obtained from Aldrich. The adhesive solution was applied to a freshly corona treated LDPE film and the solvent was allowed to evaporate for 20 min prior to lamination to a second piece of corona treated LDPE film at a temperature of 60°C and nip pressure of  $1.17 \times 10^{-2}$  kgm<sup>2</sup> (40 psi), using a bench-top heated roll laminator from Chemsultants International Network.

Table 2 Adhesion performance of a typical two-parts polyurethane adhesive

Examples	EATR (g/m <sup>2</sup> .d)	Laminate/ Coating
2-parts polyurethane adhesive (Adcote 350 A/301 A obtained from Morton)	190	LDPE/LDPE laminate

Example 3

In this example, the first in accordance with the invention, a number of commercially available polyethylenimine polymers were reacted with chloropropyltrimethoxysilane in isopropanol (IPA). The polyethylenimine polymers were taken from the EPOMIN™ range from Nippon Shokusai and the LUPASOL™ range by BASF as identified in the Tables below. In each instance the reaction product was neutralised using sodium methoxide and any sodium chloride which precipitated out of the solution was filtered off. A specific example of the process used to prepare the composition in accordance with the present invention is described below:-

A 25% solids solution of the composition in accordance with the invention was prepared by dissolving 40 g of polyethylenimine (Epomin SP-110 from Nippon Shokubai, having a molecular weight (MW) of 1000) in 143 g of HPLC grade isopropanol (IPA) obtained from Aldrich. 10g of chloropropyltrimethoxysilane (CPTMS) was added and the



solution was heated to reflux for 24 hours to complete reaction. The resulting solution was neutralised with 9g of 30% sodium methoxide solution in methanol and the resulting sodium chloride precipitate was filtered off.

5        The resulting solution was either coated onto an LDPE sample and cured or was used as a laminate adhesive. A specific example of the process used when using the composition as a laminating adhesive is described below:-

10        The composition was coated onto a freshly corona treated polyethylene film, using a #3 (green) meter bar obtained from RK. The coating was dried for 30 minutes before laminating to a second layer of freshly corona treated polyethylene. Lamination of this structure was done at a temperature of 60°C and nip pressure of  $1.17 \times 10^{-2} \text{ kgm}^2$   
15        (40 psi), using a bench-top heated roll laminator from Chemsultants International Network. In the case of simple coatings as opposed to laminates, the coatings are prepared merely by coating freshly corona treated polyethylene films using a mechanical coater and a #3 (green) metering  
20        bar, both from RK.

25        The results for the above examples and a number of other similarly prepared samples give excellent EATR results and are shown below in Table 3, in which the ratios indicated in the Examples column are, in each case the ratio of the amino-functional organic polymer and reactive silane reactants present :-

Table 3: polyethylenimines reacted with  
chloropropyltrimethoxy silane (CPTMS)

Examples	EATR (g/m <sup>2</sup> .d)	Laminate/ Coating
Neutralised [Epomin SP-006 (MW 600)/ CPTMS (1:2)], 25% solids in IPA	10	simple coating
Neutralised [Epomin SP-006 (MW 600)/ CPTMS (1:2)], 25% solids in IPA	10	simple coating
Neutralised [Epomin SP-110 (MW 1000)/ CPTMS (4:1)], 25% solids in IPA	5	PE/PE laminate
Neutralised [Epomin SP-110 (MW 1000)/ CPTMS (4:5)], 25% solids in IPA	6	PE/PE laminate
Neutralised [Lupasol WF (MW 25,000)/ CPTMS (15:1)], 25% solids in IPA	15	simple coating
Neutralised [Lupasol FG (MW 700)/ CPTMS (4:3)], 25% solids in IPA	6	PE/PE laminate
Neutralised [Lupasol G100 (MW 5000)/ CPTMS (4:3)], 25% solids in IPA	5	PE/PE laminate

5 Example 4

Each result in the following example was achieved using the same ingredients and processes as described in Example 3 above with the exception of the fact that the reactive silane used was chloropropylmethyldimethoxysilane (CPMDMS).

- 10 It will be noted that similar excellent EATR results were again obtained.

Table 4 Examples of polyethylenimines reacted with chloropropylmethyldimethoxysilane (CPMDMS).

Examples	EATR (g/m <sup>2</sup> .d)	Laminate/ Coating
Neutralised [Epomin SP-110 (MW 1000)/ CPMDMS (4:1)], 25% solids in IPA	6	PE/PE laminate
Neutralised [Epomin SP-110 (MW 1000)/ CPMDMS (4:1)] , 25% solids in IPA	5	PE/PE laminate
Neutralised [Epomin SP-110 (MW 1000)/ CPMDMS (4:1)] , 25% solids in IPA	9	PE/PE laminate

5 Example 5

This Example was again achieved using the same processes as described in Example 3. However, the reactive silane used was chloropropyltriethoxysilane (CPTES), the solvent was ethanol and the neutralising agent used was sodium ethoxide.

Table 5 Polyethylenimine reacted with Chloropropyltriethoxysilane

Examples	EATR (g/m <sup>2</sup> .d)	Laminate/ Coating
Neutralised[Lupasol FG (MW 700)/ CPTES(4:3)], 25 % solids in Ethanol	9	PE/PE laminate

#### Example 6

Each result in the following example was again achieved using the same laminating process as described in Example 3. However, with respect to the method of preparation of the reaction product, no neutralisation step was required as the reactive silane was either glycidoxypropyltrimethoxysilane (GPTMS) (a) or epoxycyclohexylethyltrimethoxysilane (A-186 obtained from Witco) (b). Polymin 447 is a hydroxylated polyethylenimine obtained from BASF. A specific example of each method of preparation of the reaction product using the above two reactive silanes is provided below:-

(a) A solution was prepared by dissolving 12 g of polyethylenimine (Lupasol PR 8515 obtained from BASF, MW 700) in 72 g of absolute ethanol obtained from Vel. 12 g of glycidoxypropyltrimethoxysilane were added and the solution was stirred for 24 HOURS at room temperature to complete reaction.

(b) A solution was prepared by dissolving 60 g of polyethylenimine (Lupasol WF obtained from BASF, MW 25,000) in 210 g of absolute ethanol obtained from Vel. 10 g of epoxycyclohexylethyltrimethoxysilane (A-186 obtained from Witco) were added and the solution was stirred for 24 HOURS at room temperature to complete reaction.

Table 6 polylythylenimines reacted with  
glycidoxypropyltrimethoxysilane (GPTMS) or  
epoxycyclohexylethyltrimethoxysilane (A-186)

Examples	EATR (g/m <sup>2</sup> .d)	Laminate/ Coating
Epomin SP-110 (MW 1000)/GPTMS(4:1.2), 25% solids in Ethanol	6	PE/PE laminate
Polymin 447 (MW 2000) /GPTMS (1:1), 25% solids in Ethanol	6	PE/PE laminate
Lupasol WF (MW 25000)/ GPTMS (50:1.5), 25% solids in Ethanol	10	simple coating
Lupasol FG (MW 700)/ GPTMS (1:1), 25% solids in Ethanol	4	PE/PE laminate
Lupasol WF (MW 25000)/ A-186 (6:1), 25% solids in Ethanol	14	simple coating
Triethylenetetramine (TETA)/A-186 (3:5), 25% solids in Ethanol	11	simple coating

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#### Example 7

Each result in the following example was achieved using the same ingredients and processes as described in Example 6 apart from the fact that the reactive silane used was either  
10 methacryloxypropyltrimethoxysilane (MPTMS) or  
acryloxypropymethyldimethoxysilane (APTMS)

Table 7 polyethylenimines reacted with methacryloxypropyltrimethoxysilane (MPTMS) or acryloxypropymethyldimethoxysilane (APTMS)

Examples	EATR (g/m <sup>2</sup> .d)	Laminate/ Coating
Lupasol PR8515 (MW 2000)/ MPTMS (1:1), 25% solids in Ethanol	5	PE/PE laminate
Lupasol PR8515 (MW 2000)/ MPTMS (1:1.5), 25% solids in Ethanol	59	PE/PE laminate
Lupasol PR8515 (MW 2000)/ MPTMS (1:2), 25% solids in Ethanol	116	PE/PE laminate
Lupasol PR 8515 (MW 2000)/ APTMS (1:1.5), 25% solids in Ethanol	145	PE/PE laminate

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#### Example 8

In this example, commercially available polyethylenimine polymers were reacted with chloropropyltrimethoxysilane in isopropanol (IPA) neutralised and mixed with a polar additive glycidol. A specific example of the process undertaken is provided below;-

A solution was prepared by dissolving 40g of polyethylenimine (SP-110 obtained from Nippon Shokubai, MW 1000) in 90g of 2-propanol obtained from Vel. 50g of chloropropyltrimethoxysilane were added and the solution was stirred at reflux temperature for 24 hours to complete the reaction. 170g of the solution were then mixed with 43g of sodium methoxide(30% solids in methanol) and stirred for one hour at room temperature. The sodium chloride precipitate was then removed by centrifugation at 3000 rpm, using a Heraeus Megafuge 1.0 centrifuge. 20g of the centrifuged

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solution was then diluted with 12.56g of isopropanol to obtain a final solution at 255 solids. 0.2g of glycidol was added to 10g of the above solution and the mixture was stirred at room temperature for 24 hours before coating.

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Table 8 Reaction Products with polar additives

Examples	EATR (g/m <sup>2</sup> .d)	Laminate/coating
[Neutralised SP-110 (MW 1000)/ CPTMS]/ Glycidol (4:5:0.72) , 25% solids in IPA	5	PE/PE laminate
[Neutralised SP-110 (MW 1000)/CPTMS]/Glycidol (4:5:1.44), 25% solids in IPA	5	PE/PE laminate

Example 9

10 Each result in the following example was achieved using the same ingredients and processes as described in Example 6 but an additional crosslinker was added to the composition subsequent to the preparation of the reaction product. A specific example follows:-

15 A solution was prepared by dissolving 2g of polyethylenimine (Lupasol FG obtained from BASF, MW 800) in 18g of absolute ethanol. 2g of glycidoxypropyltrimethoxysilane were added followed by 1g of hexanediol diacrylate crosslinker. The mixture was stirred  
20 for 20 minutes at room temperature and the resulting solution was used to coat freshly corona treated polyethylene films using a mechanical coater and a #3 (green) metering bar, both from RK.

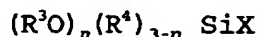
Table 9 Reaction products with additional cross-linking agents

Examples	EATR (g/m <sup>2</sup> .d )	Laminate/ Coating
Lupasol FG (MW 700) / GPTMS/butanediol diglycidylether (2:2:1), 20% in Ethanol	11	coating
Lupasol FG (MW 700) / GPTMS / glycidyl methacrylate (2:2:1), 20% in Ethanol	15	coating
Lupasol FG (MW 700) / GPTMS /hexanediol diacrylate (2:2:1), 20% in Ethanol	14	coating



### CLAIMS

1) A process for treating a surface of a substrate with a composition comprising:-  
the reaction product of an amino-functional organic polymer comprising units of the formula  $-R^2 - N(R^1)_2$  and/or units of the formula  $R^1 - N(R^2-)_2$ , wherein  
each  $R^1$  is the same or different and represents a radical selected from the group consisting of hydrogen, alkyl, hydroxy alkyl, aryl substituted hydroxy alkyl, aryl, arylalkyl, and alkylaryl, and each  $R^2$  is the same or different and represents a radical selected from the group consisting of linear or branched alkylene groups having 1 to 18 carbon atoms and arylene groups having from 6 to 18 carbon atoms, and  
a reactive silane or a mixture of reactive silanes of the formula:



where each  $R^3$  group is the same or different and represents a radical selected from the group consisting of an alkyl group having from 1 to 4 carbon atoms and an acyl group  $(RC(O)-)$  having from 1 to 4 carbon atoms, each  $R^4$  group is the same or different and represents a hydrocarbon group with from 1 to 8 carbon atoms, X represents an organic radical having at least one functional unit selected from the group of an epoxide, an aldehyde, an episulphide, an acrylate, a methacrylate, an acrylamide, a methacrylamide, an isocyanate, an isothiocyanate, a halogen atom and an acid chloride and  $n$  is 1, 2 or 3, in a non-aqueous solvent, wherein said composition does not include an ethylenically unsaturated acid; said process comprising applying the composition on to the surface to form a layer and curing the layer in the presence of moisture.

- 2) A process in accordance with either claim 1 or 2 wherein the amino-functional organic polymer is a polyethylenimine.
- 3) A process in accordance with any preceding claim wherein the reactive silane is selected from the group consisting of: gamma-acryloxypropyl trimethoxysilane, gamma-methacryloxypropyl trimethoxysilane, 3-glycidoxypropyl trimethoxysilane, chloropropyl trimethoxysilane, chloropropyl triethoxysilane, chloropropyl methyl dimethoxy silane, chloropropyl ethyldimethoxy silane, epoxycyclohexylethyltrimethoxysilane, gamma trimethoxysilylpropyl glycidyl ether and glycidoxypropyl methyldimethoxy silane.
- 4) A process in accordance with any preceding claim wherein the solvent is selected from the group consisting of methanol, ethanol and isopropyl alcohol.
- 5) A process in accordance with any preceding claim wherein the reaction product further comprises an additional crosslinker selected from the group of a further reactive silane as described in claim 1, multifunctional acrylates or methacrylates, epoxides, isocyanates, thiocyanates, acid halides, acid anhydrides, esters, alkyl halides and aldehydes, and combinations thereof.
- 6) A process in accordance with any preceding claim wherein the composition further comprises an additive selected from the group consisting of an antiblock and slip aid, a polar additive, and a wetting agent.
- 7) A process in accordance with any preceding claim wherein the substrate is selected from the group consisting of polyolefins, including oriented polypropylene (OPP), cast polypropylene, polyethylene and polyethylene copolymer; polystyrene; polyesters, including polyethylene terephthalate

(PET), or polyethylene naphthalate (PEN); polyolefin copolymers, including ethylene vinyl acetate, ethylene acrylic acid and ethylene vinyl alcohol (EVOH), polyvinylalcohol and copolymers thereof; polyamides, including nylon, and MXD6; polyimides; polyacrylonitrile; polyvinylchloride; polyvinyl dichloride; polyvinylidene chloride; polyacrylates; ionomers; polysaccharides, including regenerated cellulose; silicone, including rubbers or sealants; natural or synthetic rubbers; glassine or clay coated paper; paper board; craft paper; and metallised films and vapor deposited metal oxide coated polymer films, including  $AlO_x$ ,  $SiO_x$ , or  $TiO_x$ .

- 8) A process in accordance with any preceding claim wherein the layer is contacted with a second substrate, before the layer is fully cured, to form a laminate.
- 9) A process in accordance with any preceding claim wherein the layer is cured by heating at a temperature of from 60 to 110°C in the presence of moisture.
- 10) A coated substrate obtainable by the process in accordance with any preceding claim..
- 11) Use of the composition as described in any one of claims 1 to 6 as a gas, aroma and/or flavour barrier coating.



INVESTOR IN PEOPLE

Application No: GB 0007138.1 27/  
Claims searched: 1-11

Examiner: Martin Price  
Date of search: 10 August 2000

## Patents Act 1977 Search Report under Section 17

### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.R): C3V - VABF, VACF, VACM

Int CI (Ed.7): C08G, C09D

Other: Online - WPI, EPODOC, PAJ, CAS ONLINE

### Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	WO 98/31719 A1 (EG Technology) - see eg the claims	
A	WO 98/31539 A1 (UCB Films) - see eg the claims	
A	WO 86/07072 A1 (SCM) - the whole document	
A	US 5120363 (PPG) - see eg column 4 lines 24-66	

X Document indicating lack of novelty or inventive step  
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P Document published on or after the declared priority date but before the filing date of this invention.  
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